

**THE FOLLOWING ARE THE ENGLISH TRANSLATION
OF ANNEXES TO THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT (ARTICLE 34):**

Amended Specification (Pages 1-7)

JC09 Rec'd PCT/PTO 13 OCT 2009

1

Method for hydrogenating methylol alkanals

The present invention relates to a process for the catalytic hydrogenation of methylol-alkanals in the liquid phase over a hydrogenation catalyst at a pH of the hydrogenation
5 feed which has been set to from 6.3 to 7.8 by addition of tertiary amine.

The catalytic hydrogenation of carbonyl compounds such as aldehydes for preparing simple and functional alcohols occupies an important position in the production streams of the basic chemicals industry. This is particularly true of the hydrogenation of
10 aldehydes which are obtainable via the oxo process or aldol reaction.

The aldol reaction of alkanals with excess formaldehyde in the presence of stoichiometric amounts of base produces methylolalkanals. The use of inorganic hydroxides such as sodium hydroxide or calcium hydroxide as base is known from
15 WO 01/51438. WO 98/28253 describes amines as basic catalysts in the aldol reaction and WO 98/29374 describes basic ion exchangers for this purpose. In these processes, the methylolalkanal is obtained as a 20-70% strength by weight aqueous solution. The pH of this aqueous solution is only 3.5-6.0, since the basic catalyst used for the aldol reaction also catalyzes the Cannizzaro reaction of formaldehyde to form
20 formic acid which in turn at least partly neutralizes the base.

If polyhydric alcohols such as pentaerythritol, neopentyl glycol or trimethylolpropane are to be prepared from aqueous methylolalkanal solutions, these solutions have to be
25 hydrogenated.

This hydrogenation is generally carried out at above 80°C. Redissociation of the methylol group to the free aldehyde and also ether, ester and acetal formation are observed in the hydrogenation reactor. These secondary reactions lead to low
30 hydrogenation selectivities and to low yields of the polyhydric alcohols.

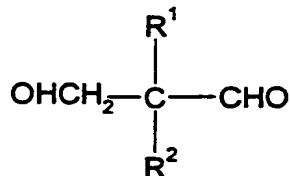
In addition, many hydrogenation catalysts are not stable under these conditions. Catalysts based on oxides of aluminum and silicon in particular, as are known from EP-A 44 444 and WO 95/32171, lose at least some of the hardness in these aqueous methylolalkanal solutions under hydrogenation conditions due to leaching of silicon
35 dioxide and in the worst case become unusable.

It is an object of the present invention to provide a process for the catalytic hydrogenation of methylolalkanals in which redissociation of methylolalkanals formed is largely suppressed, the formation of ethers, esters and acetals is largely prevented and
40 a positive effect is exerted on the mechanical stability of the catalyst. In addition, the

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process should make it possible to obtain polyhydric alcohols with good hydrogenation selectivities and in good yields.

We have found that this object is achieved by a process for the catalytic hydrogenation
5 of methylolalkanal of the formula



10 where R^1 and R^2 are each, independently of one another, a further methylol group or an alkyl group having from 1 to 22 carbon atoms or an aryl or aralkyl group having from 6 to 33 carbon atoms, in the liquid phase over a hydrogenation catalyst, wherein the pH of the hydrogenation feed is set to from 6.3 to 7.8 by addition of at least one tertiary amine.

15 The hydrogenation feed referred to in the present patent application is an aqueous solution comprising a methylolalkanal of the formula I, in particular an aqueous solution comprising from 20 to 80% by weight of methylolalkanal. Such a hydrogenation feed is preferably prepared as described in WO 98/28253 by condensation of aldehydes with
20 formaldehyde.

In this reaction, the aldehyde is reacted with from 2 to 8 times its amount of formaldehyde in the presence of a tertiary amine (aldol formation) and the reaction mixture is separated into two solutions of which one comprises the methylolalkanal mentioned and the other comprises unreacted starting material. The latter solution is
25 returned to the reaction. The fractionation is achieved by distillation or by simple separation of the aqueous phase from the organic phase. The aqueous solution comprising the methylolalkanal can be used as hydrogenation feed in the process of the present invention.

30 However, it is also possible to prepare the aqueous methylolalkanal solution as hydrogenation feed by other processes of the prior art, for example by the processes known from WO 01/51438, WO 97/17313 and WO 98/29374.

In a preferred variant of the process of the invention, an aqueous methylolalkanal solution which is particularly low in formaldehyde or is free of formaldehyde is used as
35 hydrogenation feed. In a methylolalkanal solution referred to as low in formaldehyde,

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the formaldehyde content is less than 5% by weight. Formaldehyde can be separated off from the output from the aldol formation reaction, which has been obtained, for example, as described in WO 98/28253, by methods known from the prior art, for example by distillation.

5

The methylolalkanal of the formula I is preferably a dimethylolalkanal, pentaerythrose or hydroxypivalaldehyde.

10

The hydrogenation feed is mixed with tertiary amine upstream of the inlet of the hydrogenation reactor until the hydrogenation feed has a pH of from 6.3 to 7.8. It is also possible to feed the hydrogenation feed and the tertiary amine separately into the reactor and mix them there.

15

Suitable tertiary amines are, for example, the amines listed in DE-A 25 07 461.

Preferred tertiary amines are tri-n-C₁-C₄-alkylamines, particularly preferably trimethylamine, triethylamine, tri-n-propylamine and tri-n-butylamine.

20

Amines are particularly advantageous for adjusting the pH, since they form thermally decomposable salts with formic acid so that the salts can be dissociated again after the hydrogenation. In this way, a salt as coproduct can be avoided and the tertiary amine can be returned to the process.

25

It is particularly advantageous to use the same tertiary amine in the aldol formation process which produces the methylolalkanal, viz. the condensation of a higher aldehyde and formaldehyde, and in the hydrogenation. The pH is measured by known methods, preferably by means of a glass electrode and by pH meter.

30

Catalysts which can be used for the purposes of the present invention are catalysts which are suitable for hydrogenations and preferably comprise at least one metal of transition groups 8 to 12 of the Periodic Table of the Elements, e.g. Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, preferably Fe, Co, Ni, Cu, Ru, Pd, Pt, particularly preferably Cu, preferably on a customary support material, particularly preferably on a support material comprising oxides of titanium, zirconium, hafnium, silicon and/or aluminum. The catalysts which can be used according to the present invention can be prepared by methods known from the prior art for preparing such supported catalysts. Preference is also given to using supported catalysts which comprise copper on an Al₂O₃- or TiO₂-containing support material in the presence or absence of one or more of the elements magnesium, barium, zinc or chromium. Such catalysts and their preparation are known from WO 99/44974.

35

Copper-containing supported catalysts as described, for example, in WO 95/32171 and the catalysts disclosed in EP-A 44 444 and DE 19 57 591 are also suitable for the hydrogenation according to the present invention.

- 5 The hydrogenation can be carried out batchwise or continuously, for example in a tube reactor which is charged with a catalyst bed and in which the reaction solution is passed over the catalyst bed in, for example, the downflow or upflow mode, as described in DE-A 19 41 633 or DE-A 20 40 501. It may be advantageous to recirculate a substream of the reactor output, if appropriate with cooling, and pass it over the fixed
10 bed of catalyst again. It can likewise be advantageous to carry out the hydrogenation in a plurality of reactors connected in series, for example in from 2 to 4 reactors, with the hydrogenation reaction being carried out to only a partial conversion of, for example, from 50 to 98% in the individual reactors upstream of the last reactor and the hydrogenation being completed only in the last reactor. It can be advantageous to cool
15 the hydrogenation output from the preceding reactor before it enters the next reactor, for example by means of cooling facilities or by injection of cold gases, e.g. hydrogen or nitrogen, or by introducing a substream of cold reaction solution.

The hydrogenation temperature is generally in the range from 50 to 180°C, preferably
20 from 90 to 140°C. The hydrogenation pressure employed is generally from 10 to 250 bar, preferably from 20 to 120 bar.

The hydrogenation can be carried out with addition of an inert solvent. Solvents which can be used include cyclic ethers such as THF or dioxane and also acyclic ethers,
25 likewise lower alcohols such as methanol, ethanol or 2-ethylhexanol.

Otherwise, any hydrogenation methods can be employed and it is possible to use any hydrogenation catalysts as are customary for the hydrogenation of aldehydes and are described in detail in the standard literature.

30

Example 1

Hydrogenation of hydroxypivalaldehyde to neopentyl glycol

Hydrogenation feed

- 35 1.1 mol of isobutyraldehyde were stirred with 1 mol of formaldehyde in the form of a 40% strength solution and 4 mol% of trimethylamine, based on isobutyraldehyde, at 75°C for 1 hour. The reaction solution was concentrated by distilling off low boilers such as isobutyraldehyde and part of the water under atmospheric pressure. The bottoms obtained comprised 75% by weight of hydroxypivalaldehyde, 20% by weight of
40 water and about 5% by weight of other organic secondary components.

Catalyst used

Catalyst G as described in WO 95/32171 was used.

5 Hydrogenation

The mixture described above as hydrogenation feed served as starting solution. This mixture was brought to the pH indicated in each case in table 1 by addition of trimethylamine and was pumped over the catalyst in a hydrogenation reactor with circulation of liquid (recycle:feed = 10:1) at a weight hourly space velocity of 0.3 kg_{HPA}/l_{cat} × h at 40 bar and 125°C in the downflow mode. The conversion was completed in an after-reactor operated in a single pass at 40 bar and 125°C.

A comparison of the process of the present invention with comparative examples 1 and 2 in which the pH of the hydrogenation feed was in each case outside the range specified according to the present invention is shown in table 1.

The pH was measured using a Knick model 766 pH meter provided with a glass electrode N1041A from Schott.

20 Table 1:

Ex.	pH	HPA ² [GC % by weight]	NPG ³ [GC % by weight]	i-BuOH ⁴ [GC % by weight]	HPN ⁵ [GC % by weight]	Acetal ⁶ [GC % by weight]	Selectivity
C1	5.3 ¹	0.03	91.97	2.63	0.92	0.43	96.71
1	7.4	0.02	93.04	2.10	0.90	0.11	97.83
C2	8.3	0.07	91.89	3.08	1.04	0.09	96.62

¹ without addition of amine

² HPA = hydroxypivalaldehyde

³ NPG = neopentyl glycol

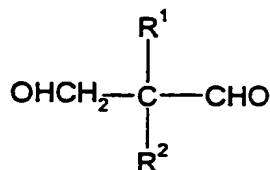
⁴ i-BuOH = isobutyl alcohol

25 ⁵ HPN = neopentyl glycol ester of hydroxypivalic acid

⁶ Acetal = hydroxypivalaldehyde NPG acetal

We claim:

1. A process for the catalytic hydrogenation of methylolalkanals of the formula



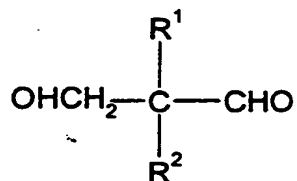
- 5 where R¹ and R² are each, independently of one another, a further methylol group or an alkyl group having from 1 to 22 carbon atoms or an aryl or aralkyl group having from 6 to 33 carbon atoms, in the liquid phase over a hydrogenation catalyst, wherein the pH of the hydrogenation feed is set to from 6.3 to 7.8 by
- 10 addition of at least one tertiary amine.
2. The process according to claim 1, wherein the hydrogenation feed contains less than 5% by weight of formaldehyde.
- 15 3. The process according to claim 1 or 2, wherein a tri-n-alkylamine is used.
4. The process according to any of claims 1 to 3, wherein trimethylamine, triethylamine, tri-n-propylamine and/or tri-n-butylamine is/are used.
- 20 5. The process according to any of claims 1 to 4, wherein the hydrogenation catalyst comprises at least one metal of transition groups 8 to 12 of the Periodic Table of the Elements.
- 25 6. The process according to any of claims 1 to 5, wherein the hydrogenation catalyst is a supported catalyst.
7. The process according to claim 6, wherein the oxides of titanium, zirconium, hafnium, silicon and/or aluminum are used as support material.
- 30 8. The process according to any of claims 5 to 7, wherein the hydrogenation catalyst comprises copper on an Al₂O₃- or TiO₂-containing support material in the presence or absence of one or more of the elements magnesium, barium, zinc and chromium.
- 35 9. The process according to any of claims 1 to 8, wherein the methylolalkanal which is hydrogenated is hydroxypivalaldehyde, pentaerythrose or dimethylolbutanal.

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Method for hydrogenating methylol alkanals

Abstract

- 5 Process for the catalytic hydrogenation of methylolalkanals of the formula



- 10 where R¹ and R² are each, independently of one another, a further methylol group or an alkyl group having from 1 to 22 carbon atoms or an aryl or aralkyl group having from 6 to 33 carbon atoms, in the liquid phase over a hydrogenation catalyst, wherein the pH of the hydrogenation feed is set to from 6.3 to 7.8 by addition of at least one tertiary amine.

PATENT COOPERATION TREATY

PCT

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

BASF AKTIENGESELLSCHAFT
67056 Ludwigshafen
Germany

Date of mailing (day/month/year) 25 May 2004 (25.05.2004)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 0000054460	
International application No. PCT/EP2004/003951	International filing date (day/month/year) 14 April 2004 (14.04.2004)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 16 April 2003 (16.04.2003)
Applicant BASF AKTIENGESELLSCHAFT et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
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<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
16 April 2003 (16.04.2003) ✓	103 17 543.1 ✓	DE	13 May 2004 (13.05.2004) ✓

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.89.70	Authorized officer Elisabeth KÖNIG (Fax 338 8970) Telephone No. (41-22) 338 8748
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/003951

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C29/141 C07C31/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92/22521 A (ARISTECH CHEMICAL CORP) 23 December 1992 (1992-12-23) claims 1-12; examples 17-19	1-9
A	EP 0 522 368 A (ARISTECH CHEMICAL CORP) 13 January 1993 (1993-01-13) claims 1-29; examples 1-8	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the International search

3 August 2004

Date of mailing of the International search report

30/08/2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/003951

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